Life and times of the Proterozoic McArthur–Yanliao Gulf: Update on the ARC-Industry–NTGS Linkage Project

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The greater McArthur Basin covers a wide extent of northern Australia, spanning from Western Australia to Queensland and stretching from near Tennant Creek in the south to an unknown extent beneath the Arafura Sea to the north. There are similarities in chemostratigraphy (eg Kunzmann *et al* 2019) and lithologies between the greater McArthur Basin and the Proterozoic sequences that crop out in North China (where they are best exposed in the so-called Yanliao Aulacogen). Recent palaeomagnetic work undertaken at Curtin University supports this link (Kirscher *et al* in press) and has led to our suggestion of the epicontinental sea forming a major McArthur–Yanliao Gulf in Nuna/Colombia (**Figure 1**). As such, a consortium of universities, industry and the Northern Territory Government obtained a three-year Australian Research Council Linkage grant to research both tectonic and palaeo-environmental importance of the basin. The grant allows the consortium to focus on unravelling the history of the basin leading to improved understanding of the tectonic evolution of Australia at

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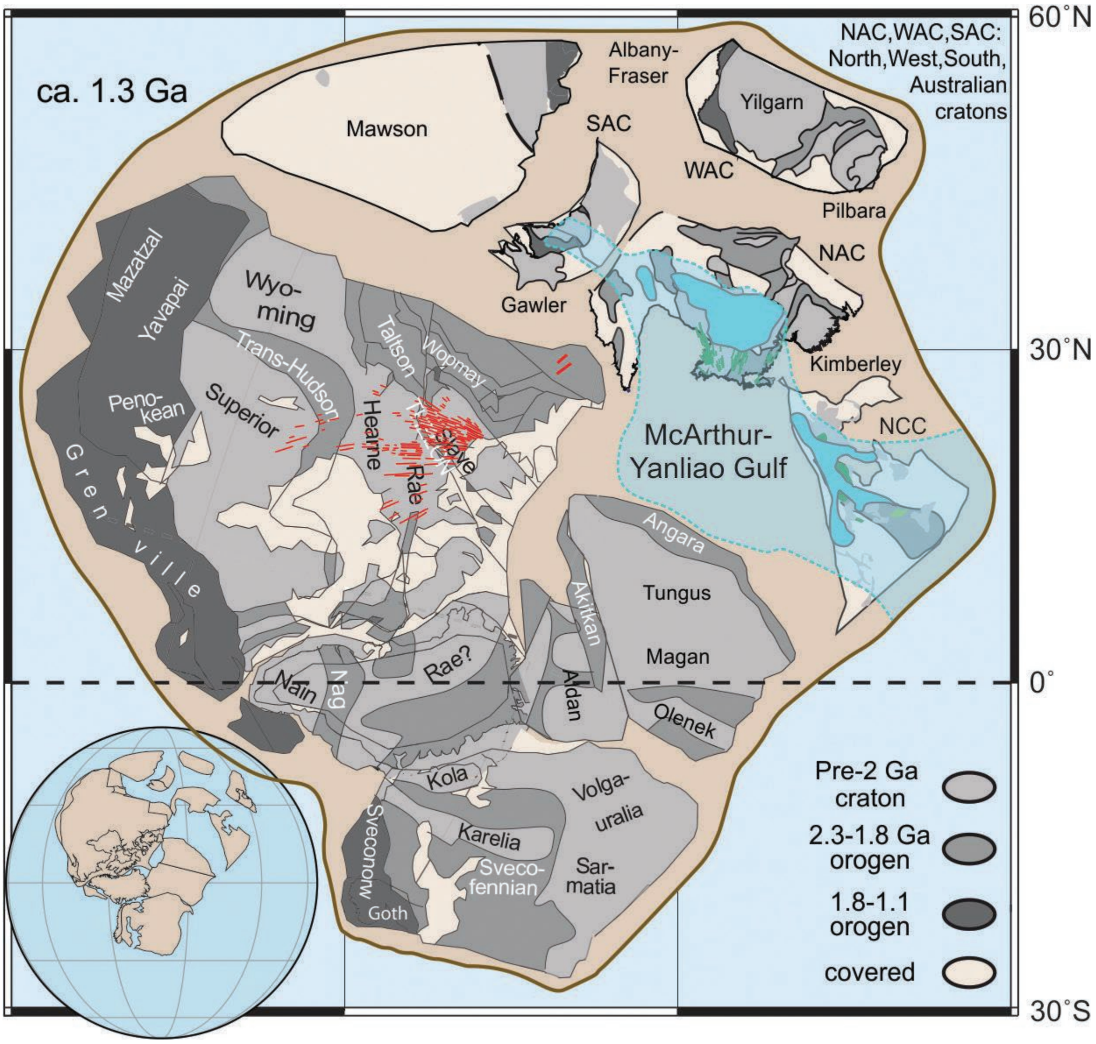

Figure 1. Tectonic assemblage map at ca 1.3 Ga. Green lines are dykes and sill associated with the ca 1.3 Ga Derim Derim–Galiwinku–Yanliao Large Igneous Province. Red lines are the ca 1.27 Ga Mackenzie dykes. Map modified from Kirscher *et al* (in review), Cox *et al* (in review).

the time, as well as that of the setting, origin and controls on the formation of the petroleum resources within the basin. In addition, the basin spans the Palaeoproterozoic–Mesoproterozoic, a fascinating time when eukaryotes gained a foothold and oxygenation of the atmosphere and ocean commenced. Consequently, the basin is an essential geological archive for global earth system development through this time period.

The partners in this project are the Australian Research Council, the Northern Territory Geological Survey (NTGS), Origin Energy Limited, Santos Limited, Imperial Oil and Gas Limited, The University of Adelaide, The University of Wollongong, The University of South Australia, and the Czech Academy of Sciences. The consortium's philosophy is to identify new data to complement existing datasets and to build a spatial and temporal framework of the chemostratigraphy, age, detrital chronology, and low-temperature thermochronology of the basin. These data will be used to: a) correlate effectively between sequences and boreholes up to 1000 km apart; b) illuminate the tectonic evolution of the basin and its margins by examining source-to-sink pathways for sediments through time; c) determine the palaeo-environmental conditions that persisted during deposition using geochemical proxies for redox, biological activity and nutrient influx; and d) study the thermal history of the basin by using low temperature thermochronometers to examine both the basin and the surrounding basement to better understand the ancient surface movements.

Over 2018, we have graduated four Honours students focussed on this project, have had several manuscripts published or placed in the publication pipeline (see references), and have undertaken three projects described below (the details of which are on the posters in the AGES 2019 foyer).

a. Detrital zircons from the Palaeoproterozoic Redbank Package to the Mesoproterozoic Favenc and Wilton packages show a distinct change in dominant age peaks from the early sandstones rich in ca 1850 Ma zircon in the former to those containing ca 1760 Ma zircon in the latter. We interpret that this reflects an increased importance of the Arunta Region as a zircon source, suggesting its uplift and erosion in the early Mesoproterozoic.
b. The ca 1820 Ma Plum Tree Volcanics mark the initiation of extension in northern Australia and herald the start of the greater McArthur Basin. The volcanics have evolved, negative εNd values (approximately -6), indicating crustal assimilation occurred during emplacement of the suite. REE trends of this suite show negative Nb and Sr anomalies, and positive Pb anomalies, which are interpreted to also indicate crustal contamination. We suggest that the volcanics formed as a result of active intraplate continental rifting due to plume impingement or lithospheric delamination after Pine Creek orogenesis.
c. We are also pioneering the measurement and interpretation of Cr isotope (δ^{53}Cr) values. We report the first Cr isotope data from the McArthur Basin. Samples were collected from mid-Proterozoic organic-rich carbonates of the ca 1.64 Ga Limbunya and McArthur groups. Analysed values from -0.293‰ to +1.389‰ represent the oldest documented positively fractionated δ^{53}Cr values in marine carbonate units reported. This is suggestive of fluctuating, but increasing, pO_2 at the time of a generally reducing environment.

Herein we shall focus on two of the novel projects undertaken over the year: 1) LA–ICP MS/MS Rb−Sr dating of shales and glauconites from the Roper Group (Honours project of Ms Eilidh Cassidy and research by Farkas, Blades, Collins, Cox and Dr Sarah Gilbert); and 2) isotope constraints on the redox structure of the Mesoproterozoic basin in which the Roper Group was deposited (Honours project of Ms April Shannon and research by Cox, Farkas, Blades, Collins).

1) LA–ICP MS/MS Rb−Sr dating of shales and glauconites from the Roper Group

A total of six shale samples throughout the lower Roper group and a single glauconitic sandstone sample from the Crawford Formation were sampled for *in-situ* Rb–Sr dating, a technique currently in development (Zack and Hogmalm 2016). Age data were collected using the laser ablation-triple quadrupole-ICP-MS (LA–QQQ–ICP–MS) at Adelaide Microscopy where ^{87}Rb is separated from ^{87}Sr in the mass spectrometer using N_2O gas. The reaction cell that sits between two quadrapoles allows mass 67 to be isolated (^{87}Rb and ^{87}Sr), followed by a reaction with N_2O to produce $^{87}Sr^{16}O$, making a total mass of 103 and therefore allowing it to be identified from ^{87}Sr. Analyses consisted of ~90 × 75 µm laser spots along a single lamination (where available) for each sample. Data were processed in the software package Iolite version 3.0. Concordia diagrams were calculated using ISOPLOT 4.15 for Excel.

A nano-powder (MicaMg) and a phlogopite crystal (MDC) were used as standards. An average (or median) spline through MicaMg was used when processing in iolite to avoid introducing any false drift correction. A systematic error has also been discovered in the nano-powder. To cover for this, we have added an arbitrary 5% error correction to the results (Sarah Gilbert, pers comm 2018).

Shales analysed (**Table 1**) from Urapunga 5 drillhole yielded Rb–Sr ages of 1343 ± 54 Ma (Jalboi Formation), 1296 ± 54 Ma (Crawford Formation) and 1323.0 ± 55 Ma (Wooden Duck Member of the Mainoru Formation). These

Table 1. Shale samples from Urapunga 5 and Urapunga 6 that were used for Rb–Sr dating.

Stratigraphic Unit	Sample	Core	Depth (m)
Jalboi Formation	U5-139.9	BMR Urapunga 5	139.9
Derim Derim Dolerite	U5-229.6	BMR Urapunga 5	229.6
Crawford Formation	U5-329	BMR Urapunga 5	329
Mainorou (Wooden Duck Mbr)	U5-578.7	BMR Urapunga 5	578.7
Mainorou (Gibb Mbr)	U6-269.3	BMR Urapunga 6	269.3
Mantungula Formation	U6-422.1	BMR Urapunga 6	422.1

also yielded initial $^{87}Sr/^{86}Sr$ values of between 0.63 ± 0.13 to 0.816 ± 0.030. The single glauconite grain from the Crawford Formation yielded a similar initial $^{87}Sr/^{86}Sr$ ratio (0.76 ± 0.11) and an age of 1339 ± 68 Ma (MSWD = 0.89). The Derim Derim dolerite sample also yielded a similar initial $^{87}Sr/^{86}Sr$ value (0.7293 ± 0094) and an age of 1308 ± 16 Ma (MSWD = 0.45). All the samples from this drillhole yielded ages that post-date deposition but are consistent with both glauconite and shale yielding magmatic fluid-assisted recrystallisation (**Figure 2**).

Two shale samples were analysed from Urapunga 6 drillhole, which does not contain any intrusions within it. Both these shales yielded ages that are consistent with the interpreted age of deposition (Gibb Mbr, Mainoru Formation, 1528 ± 43 Ma, MSWD=0.21; Mantungula Formation, 1470 ± 120 Ma, MSWD = 0.27). These samples also yielded initial $^{87}Sr/^{86}Sr$ values of 0.7091 ± 0.0208 and 0.7088 ± 0.0178, which are within error of seawater during the Mesoproterozoic (Shields and Veizer 2002).

We suggest that this technique is at a stage where relatively imprecise ages can be determined for deposition of fresh shales that have not been recrystallised. In addition, sedimentary rocks that have been recrystallised in the presence of hydrothermal fluids can be identified, and the timing of their recrystallisation can be constrained.

2. Early Mesoproterozoic marine redox and the instability of oxic marine ecosystems

It has been a long-standing debate whether the emergence and diversification of eukaryotes is linked to levels of atmospheric pO_2, related to the availability of nutrients, a consequence of the timing of evolutionary advances, or is due to changes in ecosystem structures. The early Mesoproterozoic shales of the lower Roper Group are known to host putative eukaryotes. The organic and inorganic chemistry of these shales are interpreted to record a complex redox structure consisting of oxic surface waters along with active aerobic nitrogen cycling (**Figure 3**). Underlying these oxic surface waters, lower shoreface to upper shelf sediments record an oxygen minimum zone where both Fe and Mn are actively reduced and shuttled to the distal shelf where they are re-oxidised (**Figure 4**). As the oxidation of Mn requires molecular O_2, these deeper distal shelf regions were oxic. This redox structure is interpreted to be a direct result of a strong biological control on both O_2 production and O_2 demand.

The redox structure requires a shallow redoxcline well above storm weather wave base; consequently, regular vertical mixing of reduced waters into shallow oxic ecosystems is expected on short timescales. Therefore, an impediment to eukaryote diversification may not be the absolute concentration of oxygen in basin waters, but rather the long-term stability of such oxic ecosystems. Redoxcline depth is a function of the depth of O_2 demand, which is tightly coupled to organic carbon sinking rates. Proterozoic oceans were rich in dissolved organic matter that led to shallow redoxclines. The stabilisation of oxic ecosystems and the expansion of eukaryotes may have been due to ecological restructuring caused by the transition from dissolved to particulate organic matter, pushing O_2 demand, and the redoxcline, into deeper waters.

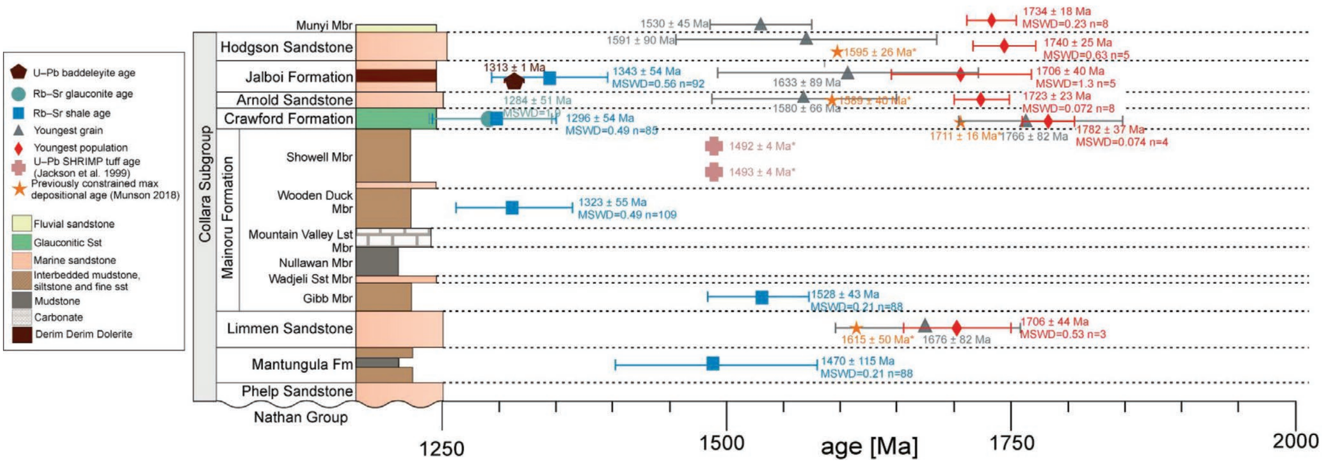

Figure 2. Compilation of U–Pb data from the lower Roper Group including baddeleyite age of the Derim Derim Dolerite (Cox *et al* 2018), Rb–Sr age of glauconite within the Crawford Formation, youngest concordant grain, youngest detrital zircon population (n=>3) along with previously published data on the Hodgson Sandstone, Arnold Sandstone, Crawford Formation and the Limmen Sandstone by Munson (2018) and U–Pb SHRIMP tuff ages from the Showell Member of the Mainorou (Jackson *et al* 1999). The maximum depositional age has been constrained by the youngest, concordant grain (red diamond) while the absolute depositional age for the Jalboi Formation, Crawford Formation, Wooden Duck Mbr (Mainorou), Gibb Mbr (Mainorou) and Mantungula Formation has been identified using Rb–Sr isotopic dating of shales within these formations and members (blue box). Fm = Formation, Mbr = Member.

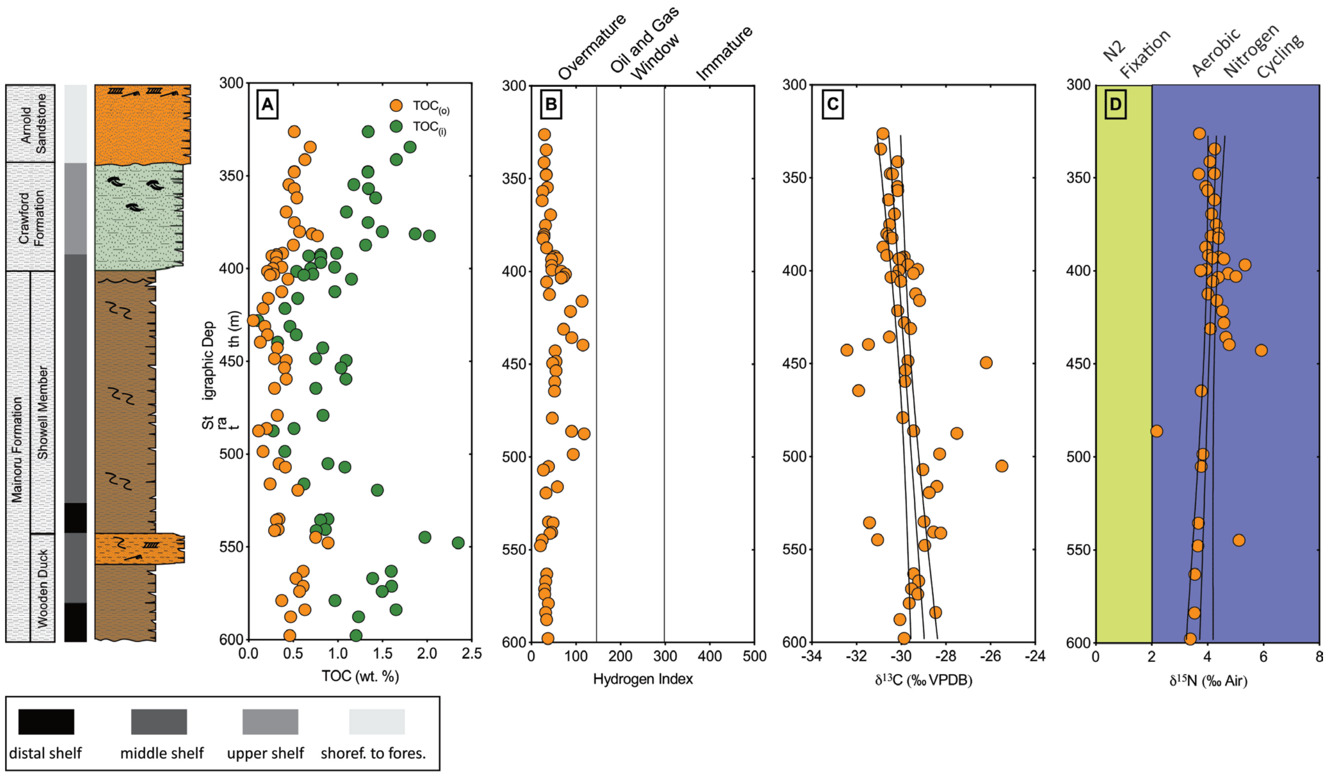

Figure 3. Organic geochemical characteristics of shale samples from Urapunga 5. (A) Measured total organic carbon (orange circles) and calculated initial organic carbon contents (green circles; following Modica and Lapierre (2012), (B) Hydrogen Index, (C) $\delta^{13}C_{org}$ and (D) $\delta^{15}N_{org}$. Black lines in (C) and (D) are linear regression (and 95% confidence interval) between the measured isotopic values and stratigraphic depth. Correlation between $\delta^{13}C_{org}$ and $\delta^{15}N_{org}$ is statistically significant at a $\alpha = 0.1$ (2-tailed p-values are 0.0019 and 0.0887 respectively). Green field in (D) is the field that can conceivably be attributed solely to N_2 fixation while the blue field in (D) are values typically associated with aerobic nitrogen cycling (Stüeken *et al* 2016).

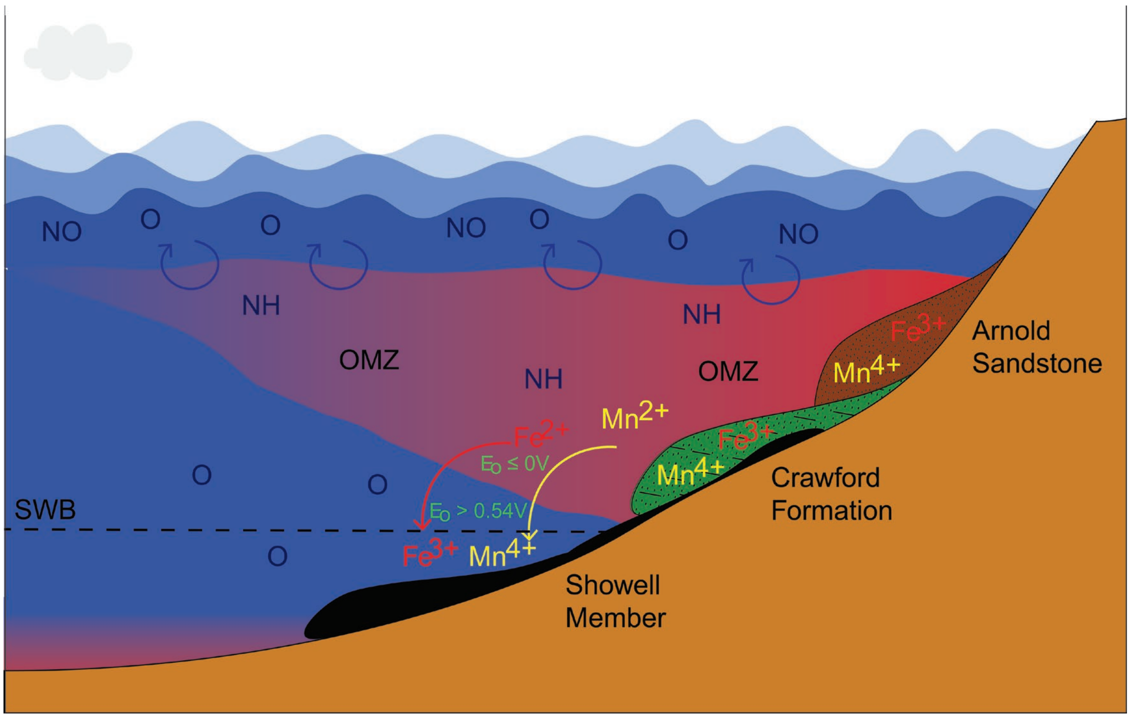

Figure 4. Schematic model of the 2D redox structure recorded by lower Roper shales. The upper layer is relatively oxic supporting aerobic nitrogen cycling. The size of the nitrate reservoir is relatively uniform from nearshore to offshore environments with no evidence for an offshore nitrate minimum. Depletions in Fe/Al and Mn/Al ratios of Arnold Sandstone and Crawford Formation shales suggests that shore face and shelf waters and sediments there were anoxic allowing both Mn and Fe to be reduced and shuttled to deeper waters. Enrichments in Fe/Al and Mn/Al ratios of Showell Member shales requires oxidation of Fe and Mn under oxidation potentials as high as the $Mn^{2+} \leftrightarrow MnO_2$ redox couplet, implying bottom water O_2 in distal shelf shales. SWB = storm weather wave base, OMZ = oxygen minimum zone.

Manuscripts published, in review or in press from these projects:

Cox GM, Jarrett A, Shannon, AV, Hall PA, Baruch ET, Hasterok D, Neilson K, Yang B, Collins AS, Blades ML and Farkas J, submitted. A very unconventional hydrocarbon play: The Roper Basin of Northern Australia. *AAPG Bulletin*.

Cox G, Sansjofre P, Blades ML, Farkas J, Collins AS, submitted. Dynamic interaction between basin redox and the biogeochemical nitrogen cycle in an unconventional Proterozoic petroleum system. *Nature Scientific Reports*.

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Zack T and Hogmalm J, 2016. Laser ablation Rb/Sr dating by online chemical separation of Rb and Sr in an oxygen-filled reaction cell. *Chemical Geology* 437, 120–133.

Popular science articles related to this study

Collins AS, Cox G and Yang B, 2017. What's Australia made of? Geologically, it depends on the state you're in. *The Conversation* 21st Nov 2017. https://theconversation.com/whats-australia-made-of-geologically-it-depends-on-the-state-youre-in-83575

Cox G and Collins AS, 2017. Ancient volcanic eruptions disrupted Earth's thermostat, creating a 'Snowball' planet. *The Conversation* 13th Sept 2017. https://theconversation.com/ancient-volcanic-eruptions-disrupted-earths-thermostat-creating-a-snowball-planet-82215 - >7K reads

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Collins AS and Merdith AS, 2017. A map that fills a 500-million year gap in Earth's history. *The Conversation* 27th June 2017. https://theconversation.com/a-map-that-fills-a-500-million-year-gap-in-earths-history-79838 - >77K reads in 24 hrs; >365K reads total. Featured in The Conversation 2017 Yearbook '50 Standout Articles from Australia's Top Thinkers'.